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Synthesis of TbO_x Nanoparticles from the Thermal Decomposition of Tb(III) Complexes*

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Terbium oxide nanoparticles, TbO_x nanoparticles, were synthesized by the thermal reaction of Tb(III) complexes as a single-source precursor with acetylacetone (acac) or hexafluoroacetylacetone (hfa). Thermal decomposition processes of Tb(III) complexes for preparation of TbO_x nanoparticles were characterized by the thermogravimetric analysis (TGA). The prepared TbO_x nanoparticles were identified using XRD and TEM measurements.
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Keywords: Lanthanides; Nanoparticles; Terbium oxide; Complex; Semiconductor

I. INTRODUCTION

Semiconductor nanoparticles have attracted considerable attention in the area of advanced materials science because of their remarkable luminescent, catalytic and magnetic properties [1-9]. Various types of preparation method of semiconductor nanoparticles have been reported for the past few decades. In particular, the thermal reaction of single-source precursor method has been utilized for the synthesis of nanoparticles in the presence of a suitable capping agent. The single-source precursor method permits to control the particle size and shape, and prevent particle aggregation by introduction of surface modification reagents. O'Brien and coworkers have synthesized CdSe nanoparticles using single-source precursor method, and successfully tuned luminescent color related to the diameter of CdSe nanoparticles, the quantum size effect [10]. Singh and coworkers have also reported synthesis of $Pd_{17}Se_{15}$ nanoparticles using Pd-Se complex and their efficient catalyst for C–O coupling reactions [11]. Recently, we have reported the synthesis of monodisperse EuS nanoparticles using Eu(III) dithiocarbamate complex, and demonstrated characteristic magneto-optical properties of EuS nanoparticles depending on their particle size, shape and surface environments [12-14].

Here, we focused on nanoparticles containing terbium ions. Various types of nanoparticles containing terbium ions, for example, terbium-doped yttrium aluminum garnet (YAG:Tb) nanoparticles [15], terbium-doped ZnO nanoparticles [16] and $TbPO_4$ nanoparticles [17], have been reported. They exhibit characteristic optical and magnetic properties based on the degenerate 4f orbitals in terbium ions. Terbium oxide (TbO_x) nanoparticles have also been reported [18, 19]. Chen and coworkers have reported synthesis of Tb_2O_3 nanoparticles by the method of pulsed-laser beam ablation at the interface of Tb_2O_3 target with acetylacetone (acac) and 2,2'-bipyridyl (bpy) molecules [20]. The acac and bpy molecules show effective coordination ability as an organic ligand for single-source precursor. Dickerson and coworkers have used the thermal decomposition of single-source precursor, terbium oleate, at 350°C for preparation of monodisperse Tb_2O_3 nanoparticles [21].

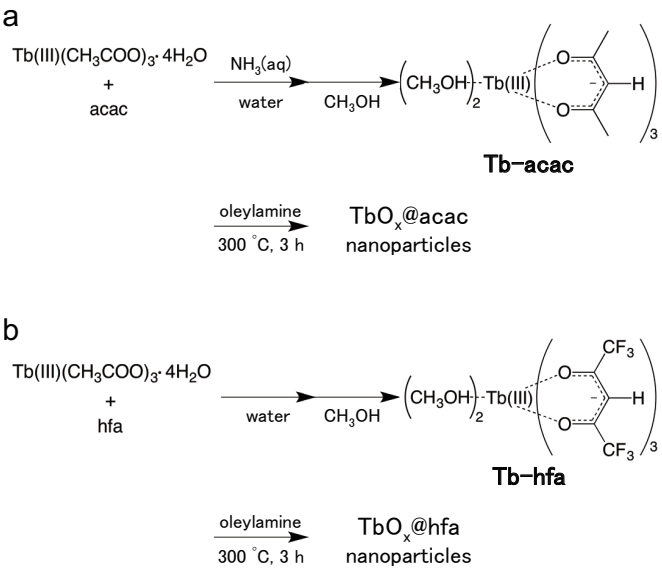

FIG. 1. Reaction schemes of (a) TbO_x@acac and (b) TbO_x@hfa nanoparticles.

In this study, we have attempted to synthesize terbium oxide nanoparticles using the thermal decomposition of terbium(III) complexes as a single-source precursor, tris(acetylacetonato)dimethanolterbium(III) ($Tb(III)(acac)_3(CH_3OH)_2$, Tb-acac) and tris(hexafluoroacetylacetonato)dimethanolterbium(III) ($Tb(III)(hfa)_3(CH_3OH)_2$, Tb-hfa) (Fig. 1). Terbium oxide nanoparticles composed of Tb(III) or (IV) ions, TbO_x nanoparticles, were synthesized by the thermal reactions of Tb(III) complexes in oleylamine at 300°C. Thermal decomposition processes of Tb(III) complexes for preparation of TbO_x nanoparticles were characterized by the thermogravimetric analysis (TGA). The prepared

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TbO_x nanoparticles were identified using XRD and TEM measurements. In the present study, we report on the influence of coordination ability of ligand for formation of TbO_x nanoparticles.

II. EXPERIMENTAL

A. Materials

Terbium(III) acetate tetrahydrate ($Tb(III)(CH_3CO_2)_3 \cdot 4H_2O$) was purchased from Wako Pure Chemical Industry, Ltd. Acetylacetone (acac, $CH_3C(O)CH_2C(O)CH_3$), hexafluoroacetylacetone (hfa, $CF_3C(O)CH_2C(O)CF_3$) and oleylamine were obtained from Tokyo Chemical Industry Co., Ltd. All other chemicals and solvents were reagent grade and were used without further purification.

B. Synthesis of precursor

1. *Synthesis of $[Tb(acac)_3(CH_3OH)_2]$, Tb-acac*

Terbium(III) acetate tetrahydrate (5.00 g, 12.3 mmol) was dissolved in distilled water (40 mL) by stirring. Acetylacetone (3.74 g, 37.4 mmol) was added dropwise to the above solution. The pH value of this solution was adjusted at pH 7 by adding NH_3 aqueous solution. The mixture produced a white precipitate after stirring for 3 h. The resulting precipitate was separated by filtration and washed 2 times with distilled water. Reprecipitation form methanol gave a white precipitate of $[Tb(acac)_3(CH_3OH)_2]$. IR (ATR): νbar = 1650(C = O), 1390($-CH_3$), 1020($-CH_3$), 920(C$-$CH$_3$) cm^{-1}; ESI-MS: m/z: calcd for $C_{12}H_{22}O_6Tb$ $[M-(acac)]^+$: 421.07; found: 421.10.

2. *Synthesis of $[Tb(hfa)_3(CH_3OH)_2]$, Tb-hfa*

Terbium(III) acetate tetrahydrate (5.00 g, 12.3 mmol) was dissolved in distilled water (40 mL) by stirring. Hexafluoroacetylacetone (7.78 g, 37.4 mmol) was added dropwise to the above solution. The mixture produced a white green precipitate after stirring for 3 h. The resulting precipitate was separated by filtration and washed 2 times with distilled water. Reprecipitation form methanol gave a white precipitate of $[Tb(hfa)_3(CH_3OH)_2]$. IR (ATR): νbar = 1650 (C = O), 1255-1141 (C $-$ F) cm^{-1}; ESI-MS: m/z: calcd for $C_{12}H_{10}F_{12}O_6Tb$ $[M - (hfa)]^+$: 636.95; found: 637.01.

C. Synthesis of terbium oxide (TbO_x) nanoparticles (TbO_x@acac and TbO_x@hfa)

Under N_2 atmosphere, precursor Tb(III) complex (Tb-acac or Tb-hfa, 1.02 mmol) was dissolved into oleylamine (15 mL, 45.6 mmol), and the mixture was heated at 300°C and stirred for 3 h. Then, the resulting liquid was centrifuged at 4000 rpm for 10 min. The precipitation was added to *n*-hexane (10 mL) and centrifuged at 4000 rpm for 10 min, and the clear liquid of oleylamine capped TbO_x nanoparticles was obtained.

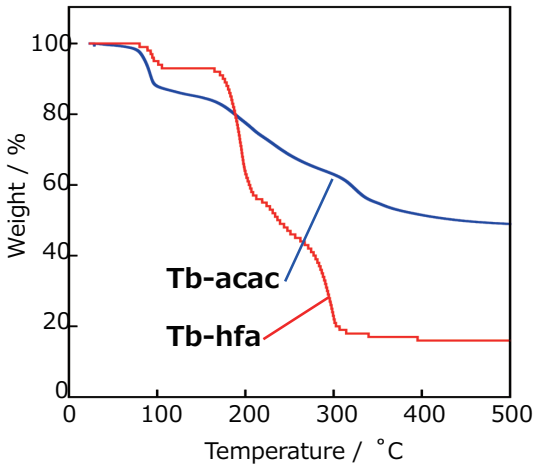

FIG. 2. Thermograbimetric profiles of Tb-acac (blue) and Tb-hfa (red).

D. Characterizations

Infrared spectra were recorded on a ThermoNicolet Avatar 320 FTIR spectrometer. Mass spectra were measured using a JEOL JMS-T100LP. High-resolution images of TbO_x nanoparticles were obtained with a TEM, JEOL 2010 FASTEM (200 kV).

III. RESULTS AND DISCUSSION

Synthesis of Tb(III) complexes, $[Tb(acac)_3(CH_3OH)_2]$ (Tb-acac) and $[Tb(hfa)_3(CH_3OH)_2]$ (Tb-hfa), were synthesized using the same method as previous reported [22] (Fig. 1). Their chemical structures were identified using IR and ESI-MS spectra. Thermogravimetric (TG) profiles of Tb(III) complexes are shown in Fig. 2. The first weight losses of Tb-acac and Tb-hfa at around 100°C(14% and 7%, respectively) are caused by the elimination of coordinated methanol molecules. The weight of Tb-acac was gradually decreased in increasing with the temperature between 100 and 500°C. In contrast, the weight of Tb-hfa was constant in the range between 100 and 150°C. We also observed that the weight of Tb-hfa was effective decreased at 150°C. These results indicate that Tb-hfa is a promising single-source precursor for preparation of terbium oxide nanoparticles at around 300°C.

TbO_x nanoparticles, TbO_x@acac and TbO_x@hfa, were synthesized by the thermal reaction of Tb-acac and Tb-hfa at 300°C, respectively (Fig. 1). The prepared powders were separated by centrifugation and washed with *n*-hexane. After washing, powder of TbO_x@acac and TbO_x@hfa were obtained. The prepared TbO_x nanoparticles were analyzed by the transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS). Figure 3a and b show TEM images of TbO_x@acac and TbO_x@hfa nanoparticles. TEM image

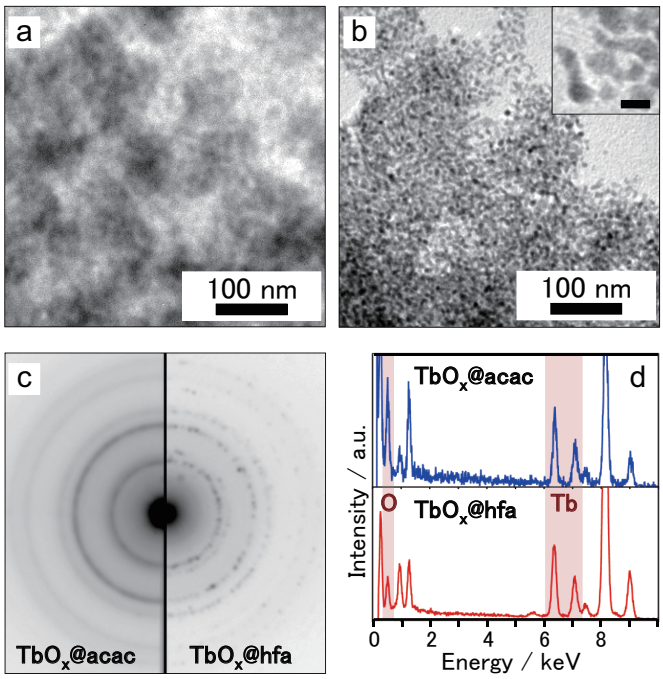

FIG. 3. TEM images of (a)TbO_x@acac and (b)TbO_x@hfa nanoparticles. Inset figure: length of scale bar = 10 nm. (c)The electron diffraction patterns of TbO_x@acac (left) and TbO_x@hfa (right) nanoparticles. (d) EDS analysis of TbO_x@acac (blue) and TbO_x@hfa (red) nanoparticles.

of TbO_x@acac nanoparticles provides cloud-liked aggregations without clear shapes. On the other hand, TEM image of TbO_x@hfa nanoparticles shows smaller spherical particles. Their average particle size was found to be 7.1 nm. The electron diffraction pattern of TbO_x@acac is the same as that of TbO_x@hfa (Fig. 3c). These electron diffraction patterns are similar to that of Tb_2O_3, Tb_4O_7 and TbO_2 compounds. EDS analysis indicates that their particles are composed of terbium and oxygen atoms (Fig. 3d). From these results, we successfully prepared TbO_x nanoparticles using single-source precursors, Tb-acac and Tb-hfa. The size and shape of TbO_x nanoparticles are dependent of the thermogravimetric data for single-source Tb(III) complex. The decomposition temperature of Tb(III) complex is directly linked to the coordination ability of the ligands. According to the previous reports, the coordination ability of the acac and hfa ligands (binding constants of lanthanide complex) is estimated to be $\log \beta_{1,\mathrm{acac}} = 8.3$ and $\log \beta_{1,\mathrm{hfa}} = 4.7$, respectively[23]. We consider that Tb(III) complex including hfa ligand with small binding constant is suitable for preparation of smaller and spherical TbO_x nanoparticles.

IV. CONCLUSIONS

TbO_x nanoparticles was successfully synthesized by the thermal decomposition of single-source precursor. The thermogravimetric profiles show that Tb-hfa was effectively decreased at 150°C and a promising single-source precursor for preparation of terbium oxide nanoparticles at around 300°C. The TEM image of TbO_x@hfa shows cloud-liked aggregations without clear shapes, in contrast, that of TbO_x@acac shows smaller spherical particles. Prepared TbO_x nanoparticles was expected to be useful for application in the field of optic and magnetic material sciences.

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